

11-28-00

A

11/27/00

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

## Patent Application Transmittal

Docket No. PER0014US

**BOX PATENT APPLICATION**  
 Assistant Commissioner for Patents  
 Washington, D.C. 20231

Crompton Corporation  
 199 Benson Road  
 Middlebury, CT 06749

Sir:

Date: November 27, 2000

Transmitted herewith for filing is the Patent Application of:

Inventors: **DENIS GHEQUIERE AND RÉMY DUMONT**  
 For: **PROCESS FOR THE MANUFACTURE OF POLYURETHANE FOAM, AMINE  
 POLYESTERPOLYOL USED IN THIS PROCESS AND FOAM OBTAINED**

Enclosed are:

\_\_\_\_\_ sheets of drawings.  
 An assignment of the invention to Crompton Corporation, Middlebury, CT 06749.  
 A certified copy of a \_\_\_\_\_ application.  
 Declaration and Power of Attorney  
 Executed.  Unexecuted.  
 Information Disclosure Statement with copies of cited references.  
 Associate Power of Attorney.  
 Certificate of translation.

JC912 U.S. PTO  
09/723034

The filing fee has been calculated as shown below:

	Claims Filed	Extra Claims	Rate	Fee
<b>Basic Fee</b>				<b>\$710.00</b>
<b>Total Claims</b>	<b>-31</b>	<b>11</b>	<b>X \$18.00</b>	<b>\$198.00</b>
<b>Independent Claims</b>	<b>-3</b>	<b>0</b>	<b>X \$80.00</b>	<b>\$</b>
<input checked="" type="checkbox"/> <b>Multiple dependent claims presented</b>			<b>+ \$270.00</b>	<b>\$</b>
<b>Total Fee</b>				<b>\$908.00</b>

Please charge Deposit Account No. **23-2656** in the amount of **\$908.00** A duplicate copy of this sheet is enclosed.

The Commissioner is hereby authorized to charge payment of the following fees associated with this communication or credit any overpayment to Deposit Account No. **23-2656**: any additional filing fees required under 37 CFR 1.16 and any patent application processing fees under 37 CFR 1.17. A duplicate copy of this sheet is enclosed.

The Commissioner is hereby authorized to charge payment of the following fees during the pendency of this application or credit any overpayment to Deposit Account No. **23-2656**: any patent application processing fees under 37 CFR 1.17 and any filing fees under 37 CFR 1.16 for presentation of extra claims. A duplicate copy of this sheet is enclosed.

## CERTIFICATE OF MAILING

I hereby certify that, on the date shown below, this correspondence is being deposited with the United States Postal Service in an envelope addressed to Box Patent Application, Assistant Commissioner for Patents, Washington, DC 20231 as "Express Mail Post Office to Addressee".

Mailing Label No. **HB355707220US**  
 on **November 27, 2000**

Name of person mailing paper

*Shirley S. Ma*

Signature

Respectfully Submitted,

By: *Shirley S. Ma*  
 Attorney: Shirley S. Ma  
 Registration No. 44,216  
 Tel.: 203-573-3313

IN THE MATTER OF NATIONAL PHASE PROCESSING  
IN : THE UNITED STATES OF AMERICA  
OF THE INTERNATIONAL PATENT APPLICATION  
PCT/FR 99/01176  
FILED ON : MAY 18, 1999  
THE INVENTION OF :  
GHEQUIERE Denis  
29, rue Madeleine Fosse  
27370 TOURVILLE LA CAMPAGNE, FRANCE

DUMONT Rémy  
37, rue du Point du Jour  
27370 THUIT SIGNOL, FRANCE

I, John Neil Albert SWEENEY BSc, PhD, Dip. Trans.IoL  
translator to RWS Group plc, of Europa House, Marsham Way, Gerrards Cross,  
Buckinghamshire, England, do hereby declare that I am well acquainted with the English and  
French languages and that the accompanying translation is a translation made by me of the  
above International Patent Application. To the best of my knowledge and belief, this is a true  
translation.



J. N. A. SWEENEY  
For and on behalf of RWS Group plc

Dated this 2<sup>nd</sup> day of November 2000

**PROCESS FOR THE MANUFACTURE OF POLYURETHANE FOAM, AMINE POLYESTERPOLYOL USED IN THIS PROCESS AND FOAM OBTAINED**

The present invention relates to a process for the manufacture of a polyurethane foam by reaction of a 5 polyol with a polyisocyanate, in which process a tertiary amine is used as catalyst and in which process an expansion agent or foaming agent, such as water, for example, is used.

It is well known to use one or more tertiary 10 amines to catalyze a first reaction: that of at least one polyol with at least one polyisocyanate. Furthermore, in the case where water is used as foaming 15 agent, the tertiary amine(s) is (are) capable of catalyzing a second reaction: that of water with the free isocyanate functional groups, which reaction results in the evolution of carbon dioxide gas which serves for the expansion of the foam. Several known 20 techniques exist for the preparation of polyurethanes. According to a first technique, at least one polyetherpolyol and/or at least one polyesterpolyol is reacted with at least one polyisocyanate, so as to obtain a prepolymer comprising free isocyanate groups, and then the prepolymer obtained is reacted with an 25 additional amount of polyol(s). Another well known technique is the so-called "one shot" technique, where all the ingredients are introduced, separately or selectively premixed according to their compatibility, 30 into the mixing head.

The known tertiary amines can promote the first 35 reaction and/or the second reaction to variable extents. When one of the reactions is not catalyzed or is insufficiently catalyzed, it is then necessary to use another catalyst for the other reaction. This other catalyst can be an organometallic derivative, such as stannous octoate or dibutyltin dilaurate, known for preferentially catalyzing the isocyanate polyol reaction. The use is therefore being attempted of tertiary amines which satisfactorily catalyze both reactions. It is known to use tertiary amines, such as

N-ethylmorpholine, dimethylbenzylamine, triethylene-diamine and hexadecyldimethylamine, these tertiary amines being introduced as such into the reaction mixture.

5        However, these tertiary amines have a disadvantage: they are volatile, have a very unpleasant amine smell and are often toxic. As most of the tertiary amine(s) remains in the foam in the free state, the foam prepared has an undesirable smell and  
10      gives off toxic vapors. Furthermore, the handling of tertiary amines during the manufacture of polyurethane foam demands specific precautions in order to meet safety standards.

15      In order to overcome the above disadvantages, the use has been proposed (paper by Savoca, Franson and Louie, UTECH'92 Conference Proceedings, p. 309-315 and US-A 4 433 170) of less volatile amines with a high molecular weight, however, the ratio by weight of the tertiary amine functional group with respect to the  
20      weight of the molecule becomes low and the reactivity of the catalyst decreases. Furthermore, these amines are more expensive, they often still have an unpleasant smell and they often have a reactivity which is too different from that of standard amines, which is not  
25      very acceptable to foam producers.

30      Furthermore, it has also been proposed (paper by Diblitz and Hoell, UTECH'92 Conference Proceedings, p. 80-85) to attach the tertiary amine catalyst to free isocyanate functional groups. To this end, a tertiary  
35      amine, for example a hydroxylated tertiary amine, which reacts with the isocyanate functional groups during the preparation of the polyurethane is added to the reaction mixture. However, in this case, it is still necessary to handle polluting amines at the stage of preparation of the foam and precautions are still necessary to meet safety standards.

The preparation of a polyurethane by reaction of at least one polyesterpolyol with at least one polyisocyanate is well known. This polyesterpolyol is

conventionally prepared by reaction of an acid reactant having a functionality at least equal to 2, such as adipic acid, with at least one polyol with a functionality equal to 2, such as diethylene glycol, 5 subsequently denoted by P2, and at least one polyol with a functionality at least equal to 3, such as trimethylolpropane, glycerol or pentaerythritol, subsequently denoted by P3. FR-A-2 747 389 discloses the manufacture of specific polyesterpolyols, capable 10 of being used in the manufacture of polyurethane foams, which do not exhibit fogging when they are used in the passenger compartment of a vehicle. According to this patent, the polyol P2 comprises monoethylene glycol and optionally a branched glycol with a functionality equal 15 to 2 and the polyol P3 is a polyoxyalkylenated polyol which is, inter alia, obtained from triethanolamine or from triisopropanolamine. In the preparation of the polyurethane foams disclosed in FR-A-2 747 389, a separate tertiary amine catalyst, dibutylbenzylamine 20 according to the examples, is still added.

According to the present invention, it has been found that, when the polyesterpolyol is prepared from at least one polyol P3 which is a polyoxyalkylenated polyol obtained by oxyalkylation of a tertiary 25 polyalkanolamine and when it is thus "amine", it is no longer essential, during the manufacture of the polyurethane foam, to separately add a tertiary amine as catalyst or, that to say the least, the amount of separate tertiary amine to be added is markedly 30 reduced. This is because it has been found that the amine polyesterpolyol defined above has an autocatalytic effect, that is to say that it has both a reactive role and a catalyst role.

Throughout the text of the present patent 35 application, the term "polyalkanolamine" has generically denoted an alkanolated amine which can be either a polyalkanolmonoamine or a polyalkanolpolyamine.

In a first embodiment, the tertiary polyalkanolamine is a polyamine, at least one amine group and preferably all the amine groups of which is (are) tertiary and is (are) substituted by identical or 5 different C<sub>1</sub>-C<sub>6</sub> alkanol radicals.

In a second embodiment, the tertiary polyalkanolamine is a tertiary monoamine substituted by identical or different C<sub>1</sub>-C<sub>6</sub> alkanol radicals.

Generally, according to the present invention, 10 it has been found that an amine polyesterpolyol in which is inserted at least one such polyoxyalkylenated polyalkanolamine had, by itself, a catalytic effect for the formation of polyurethane foams. It acts mainly on the foaming reaction in the presence of water and to a 15 certain extent on the reaction of the polyol with an isocyanate, known as gelling. Consequently, it is possible not to use any other amine catalyst, only a small amount of catalyst of the organometallic type 20 optionally being able to be added in order to accelerate the gelling reaction and to obtain a foam which does not collapse.

According to the invention, the tertiary amine is introduced during the polyesterification process into at least one polyesterpolyol used for the 25 manufacture of the polyurethane: it is thus included or inserted in the said polyesterpolyol; the result of this is that:

- the risks of evolution of tertiary amine during the manufacture of the polyurethane are avoided 30 and, consequently, there is neither a problem of odor nor a problem of toxicity on the foam production site; problems of pollution during the production of the foam are thus avoided and certain specific precautions for meeting safety 35 standards do not have to be taken;
- foams are obtained which do not have an amine smell and are less toxic. In particular, a source of fogging when the foam is used in the passenger compartment of a motor vehicle is thus avoided

and, furthermore, when polyesterpolyols, such as those disclosed in FR-A-2 747 389, not comprising volatile cyclic dimers are employed, the foam does not result in any fogging.

5 The subject matter of the present invention is consequently a process for the manufacture of a polyurethane foam by reaction of at least one polyesterpolyol and of at least one polyisocyanate in the presence of a foaming agent and of a catalyzing 10 agent, such a polyesterpolyol having been obtained beforehand by reaction of an acid reactant A, comprising at least one aliphatic or aromatic polyacid with a functionality at least equal to 2, with at least one polyol P2 with a functionality equal to 2 and at 15 least one polyol P3 with a functionality at least equal to 3 and subsequently being denoted by AP2P3, characterized in that the catalyzing agent is at least partially composed of at least one amine polyesterpolyol AP2P3, in which at least a portion of 20 the polyol P3 is composed of at least one polyoxyalkylenated polyalkanolamine having at least one tertiary amine functional group, the alkanol radicals of the said polyalkanolamine being C<sub>1</sub>-C<sub>6</sub> radicals, the alkylene oxide units being C<sub>2</sub>-C<sub>4</sub> units and the 25 statistical mean of the number N of alkylene oxide units per polyoxyalkylated polyalkanolamine molecule being equal to  $f \times x$ , f being the number of hydroxyl functional groups per polyalkanolamine molecule and x being a number between 1 and 10 inclusive, preferably 30 between 2 and 5.

The foaming agent is preferably water.

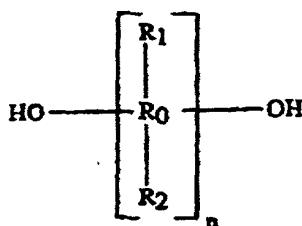
According to the invention, preferably no amine catalyst other than the amine polyesterpolyol AP2P3 is used. However, it can be advantageous to also add a 35 nonamine catalyst of organometallic type, such as stannous octoate or dibutyltin dilaurate, in order to accelerate the gelling reaction of the isocyanate with the polyol and thus to obtain a more stable foam.

The polyalkanolamine can advantageously be a polyamine, all the amine functional groups of which are tertiary; however, in a particularly preferred way, the polyalkanolamine is a tertiary monoamine.

5 Preferably, the alkanol radicals of the polyalkanolamine(s) are C<sub>2</sub>-C<sub>3</sub> radicals and the alkylene oxide units are taken from the group formed by ethylene oxide, propylene oxide and their mixtures, x being any number between 2 and 5 inclusive.

10 In the amine polyesterpolyol AP2P3, the molar ratio of the polyoxyalkylenated polyalkanolamine(s) to all the other polyols used for the reaction with the acid reactant A is preferably between 1/99 and 50/50, with greater preference between 3/97 and 10/90  
15 (proportions in moles).

15 The polyol P2 comprises at least one glycol chosen from the group formed by monoethylene glycol, diethylene glycol and polyethylene glycols with an order greater than 2; it can also comprise at least one  
20 branched glycol of formula:



in which formula:

- R<sub>0</sub> represents, independently in each [R<sub>1</sub>R<sub>0</sub>R<sub>2</sub>] unit, a carbon atom, a C<sub>6</sub> alicyclic radical, a phenyl radical or a heterocyclic radical comprising 4 to 6 atoms which is saturated or unsaturated, the heteroatom being O or N;
- R<sub>1</sub> and R<sub>2</sub> represent, independently in each [R<sub>1</sub>R<sub>0</sub>R<sub>2</sub>] unit and independently of one another, a hydrogen atom, a linear C<sub>1</sub>-C<sub>6</sub> alkyl radical, a branched C<sub>3</sub>-C<sub>6</sub> radical, a C<sub>6</sub> alicyclic radical or an aryl radical;
- with the proviso that, if R<sub>0</sub> is not a ring in any of the [R<sub>1</sub>R<sub>0</sub>R<sub>2</sub>] units, R<sub>1</sub> and/or R<sub>2</sub> is (are)

different from H in at least one of the  $[R_1R_0R_2]$  units;

5 - n is an integer between 1 and 8 (inclusive), with the proviso that, if n is greater than or equal to 4, the number of the carbon atoms in the combined  $R_0$ ,  $R_1$  and  $R_2$  radicals is greater than 8 in total.

10 Advantageously, the polyol P3 is composed entirely of one or more polyoxyalkylenated polyalkanolamine(s); however, it can also comprise at least one polyoxyalkylenated polyalkanol obtained by oxyalkylation from a hydroxylated component, such as trimethylolethane, trimethylolpropane, ditrimethylolpropane, pentaerythritol, dipentaerythritol, glycerol, hexane-1,2,6-triol, butane-1,2,4-triol, sorbitol, 15 tris(2-hydroxyethyl) isocyanurate and their mixtures, the number of alkylene oxide units per hydroxyl functional group of the polyalkanol preferably being, as a statistical mean, between 1 and 10 inclusive. The polyol P3 can also comprise non-oxyalkylenated 20 alkanols, such as trimethylolethane, trimethylolpropane, ditrimethylolpropane, pentaerythritol, dipentaerythritol, glycerol, hexane-1,2,6-triol, butane-1,2,4-triol, sorbitol, tris(2-hydroxyethyl) isocyanurate and their mixtures.

25 The acid reactant A comprises at least one aliphatic or aromatic diacid preferably taken from the group formed by adipic acid and phthalic anhydride; it can also comprise at least one branched acid having a functionality greater than or equal to 2, which 30 branched acid is preferably a dimer of an unsaturated C<sub>12</sub>-C<sub>24</sub> fatty acid. Use is advantageously made of a C<sub>18</sub> fatty acid mono-, di- and trimer mixture comprising at least 70% by weight of dimer.

35 For the preparation of the amine polyesterpolyol AP2P3, the acid reactant A is conventionally reacted with a total amount of polyols P2 and P3 greater than stoichiometry, so as to obtain an amine polyesterpolyol AP2P3 comprising at least two free hydroxyl groups per molecule. The reaction is

generally carried out under an inert atmosphere, at a temperature of between 160 and 250°C, in the presence of an appropriate metallic or organometallic catalyst.

The polyurethane foam is prepared by reaction 5 of at least one polyesterpolyol and of at least one polyisocyanate by any known process, in particular by the so-called "one shot" process. The processes for the manufacture of polyurethanes are described in J.H. Saunders, K.C. Frisch, High Polymers, 1964, Vol. 26, 10 entitled "Polyurethanes Chemistry and Technology", published by "Interscience Publishers", or in G. Woods, 1982, "Flexible Polyurethane Foams: Chemistry and Technology", published by "Applied Science Publishers".

Other additives can also be introduced in a 15 known way into the reaction mixture, such as surfactants, polyols with a low molecular weight of less than or equal to 400 as chain extenders, foam-stabilizing agents, flame-retardant agents, pigments, dyes, fillers, stabilizers against aging or substances 20 having a fungistatic or bacteriostatic effect.

The polyisocyanate used can conventionally be 25 at least one aromatic, aliphatic or heterocyclic polyisocyanate. Use is generally made of polyisocyanates or mixtures of polyisocyanates which are readily available commercially, such as 2,4- and 2,6-toluylene diisocyanate (TDI) and their mixtures, diphenylmethane diisocyanates (MDI) or prepolymers resulting from the partial reaction of a polyisocyanate with a hydroxylated compound.

Another subject matter of the invention is an 30 amine polyesterpolyol AP2P3 capable of being used in the process defined above, the said polyesterpolyol being obtained by reaction of an acid reactant A, comprising at least one aliphatic or aromatic polyacid 35 with a functionality at least equal to 2, with at least one polyol P2 with a functionality equal to 2 and at least one polyol P3 with a functionality at least equal to 3, a least a portion of the polyol P3 being composed of:

5        - at least one polyoxyalkylenated tertiary polyalkanolmonoamine, the alkanol radicals of the said polyalkanolmonoamine being C<sub>1</sub>-C<sub>6</sub> radicals, the alkylene oxide units being C<sub>2</sub>-C<sub>4</sub> units and the statistical mean of the number of alkylene oxide units per hydroxyl functional group of the polyalkanolmonoamine being between 1 and 10 inclusive, the polyol P2 in this case not comprising monoethylene glycol, or

10      - at least one polyoxyalkylenated polyalkanol-polyamine having at least one tertiary amine functional group, the alkanol radicals of the said polyalkanolpolyamine being C<sub>1</sub>-C<sub>6</sub> radicals, the alkylene oxide units being C<sub>2</sub>-C<sub>4</sub> units and the statistical mean of the number N of alkylene oxide units per polyalkanolpolyamine molecule being equal to  $f \times x$ , f being the number of hydroxyl functional groups per polyalkanolamine molecule and x being a number between 1 and 10 inclusive;

15      in this case, preferably all the amine functional groups of the polyamine are tertiary.

20      The alkanol radical of the polyalkanolamine(s) is preferably a C<sub>2</sub>-C<sub>3</sub> radical and the alkylene oxide unit is taken from the group formed by ethylene oxide, propylene oxide and their mixtures.

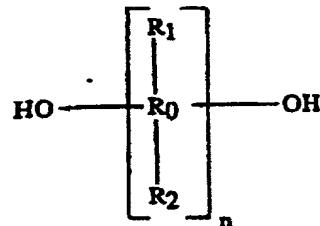
25      The molar ratio of the polyoxyalkylenated polyalkanolamine to all the other polyols used for the reaction with the acid reactant A is advantageously between 1/99 and 50/50, preferably between 3/97 and 30      10/90 (proportions in moles).

35      When the polyalkanolamine is a polyalkanolmonoamine, the polyol P2 advantageously comprises at least one glycol chosen from the group formed by diethylene glycol and polyethylene glycols with an order greater than 2.

When the polyalkanolamine is a polyalkanolpolyamine, the polyol P2 advantageously comprises at least one glycol taken from group formed

by monoethylene glycol, diethylene glycol and polyethylene glycols with an order greater than 2.

In all cases, the polyol P2 can also comprise at least one branched glycol of formula:



5

in which formula:

- $R_0$  represents, independently in each  $[R_1R_0R_2]$  unit, a carbon atom, a  $C_6$  alicyclic radical, a phenyl radical or a heterocyclic radical comprising 4 to 10 atoms which is saturated or unsaturated, the heteroatom being O or N;
- $R_1$  and  $R_2$  represent, independently in each  $[R_1R_0R_2]$  unit and independently of one another, a hydrogen atom, a linear  $C_1$ - $C_6$  alkyl radical, a branched  $C_3$ - $C_6$  radical, a  $C_6$  alicyclic radical or an aryl radical;
- with the proviso that, if  $R_0$  is not a ring in any of the  $[R_1R_0R_2]$  units,  $R_1$  and/or  $R_2$  is (are) different from H in at least one of the  $[R_1R_0R_2]$  units;
- $n$  is an integer between 1 and 8 (inclusive), with the proviso that, if  $n$  is greater than or equal to 4, the number of the carbon atoms in the combined  $R_0$ ,  $R_1$  and  $R_2$  radicals is greater than 8 in total.

25 The polyol P3 is preferably composed entirely of one or more polyoxyalkylenated polyalkanolamine(s). However, the polyol P3 can also comprise at least one polyoxyalkylenated polyalkanol obtained by oxyalkylation from a hydroxylated component, such as 30 trimethylolethane, trimethylolpropane, ditrimethylolpropane, pentaerythritol, dipentaerythritol, glycerol, hexane-1,2,6-triol, butane-1,2,4-triol, sorbitol, tris(2-hydroxyethyl) isocyanurate and their mixtures, the number of alkylene oxide units per hydroxyl 35 functional group in the molecule being, as a

statistical mean, between 1 and 10 inclusive. The polyol P3 can also comprise a non-oxyalkylenated polyol, such as trimethylolethane, trimethylolpropane, ditrimethylolpropane, pentaerythritol, dipenta-  
5 erythritol, glycerol, hexane-1,2,6-triol, butane-1,2,4-triol, sorbitol, tris(2-hydroxyethyl) isocyanurate and their mixtures.

The acid reactant A advantageously comprises at least:

10 - one aliphatic or aromatic diacid preferably taken from the group formed by adipic acid and phthalic anhydride, and/or  
- one branched acid having a functionality greater than or equal to 2, which branched acid is  
15 preferably a dimer of an unsaturated C<sub>12</sub>-C<sub>24</sub> fatty acid.

Another subject matter of the invention is the polyurethane foams obtained by the process defined above. These polyurethane foams can be used in all 20 their known uses. Mention may be made of their use in the furniture industry, for the manufacture of mattresses, cushions and coverings, for the manufacture of cushions and armrests in vehicles, and as absorbent for mineral oils. When they are rigid, they can be used 25 as thermal and sound insulators in buildings, as shockproofing in packages, as filters and, for their buoyancy, in shipbuilding. More particularly, a subject matter of the invention is the use of these foams for the production of components intended to equip the 30 passenger compartment of a motor vehicle.

Several examples of the implementation of the process according to the invention will be given below, purely by way of illustration and without limitation.

**EXAMPLES**

35 a) Preparation of ethoxylated triethanolamines (TEA)

Triethanolamine and an aqueous potassium hydroxide solution are introduced into a 6 liter reactor in the proportions given in Table I below. The

atmosphere and the contents of the reactor are dehydrated under a nitrogen atmosphere at 140°C. The reactor is closed and ethylene oxide is gradually introduced while maintaining the temperature at 150-160°C and the pressure of the reactor at at most  $3 \times 10^5$  Pa. The amount of ethylene oxide is given in Table I according to whether a triethanolamine comprising on average N = 3, 6, 9 or 12 mol of ethylene oxide, denoted respectively by TEA 3 AO, TEA 6 AO, TEA 9 AO or TEA 12 AO, is desired. The reaction mixture is kept heated for 30 minutes and then cooled before opening the reactor.

TABLE I

	TEA 3 AO	TEA 6 AO	TEA 9 AO	TEA 12 AO
TEA, g	2120	1450	1090	880
KOH (50%), g	4	4	4	4
Ethylene oxide, g	1880	2560	2900	4000
OHN (mg KOH/g)	611	425	320	243

OHN = hydroxyl number

15

Trimethylolpropane ethoxylated with 12 mol of ethylene oxide (TMP 12 AO) and glycerol ethoxylated with 12 mol of ethylene oxide (GLY 12 AO) are prepared analogously.

20 b) Preparation of polyesterpolyols

Adipic acid and the polyols are introduced, into an esterification reactor equipped with a fractionating column, in the molar proportions given in Table II, such that the finished product has a hydroxyl number (OHN) equal to  $60 \pm 2$  mg of KOH/g and an acid number (AN)  $< 2$  mg of KOH/g. The mixture is heated to 220-230°C under a nitrogen atmosphere in the presence of 40 ppm of a tin-derived catalyst, such as "Fomrez SUL 11A", manufactured by "Witco Corporation". After 25 selective distillation of the water formed, the reaction is continued until the OHN and AN values defined in Table II are obtained.

TABLE II

	A	B	C	D	E	F	G	H	I	J	K	L	M
MEG <sup>(1)</sup>								60	60		57	64	62
DEG <sup>(2)</sup>	94	94	93.5	93.5	93.5	94	94			89			
MPG <sup>(3)</sup>								35	34.5		33	30	30
TMP <sup>(4)</sup>	6									5			4
TEA <sup>(5)</sup>		6										2	
PE <sup>(6)</sup>													
TEA 3 EO			6.5										
TEA 6 EO				6.5									
TEA 9 EO					6.5						6	6	4
TEA 12 EO						6	6 <sup>(7)</sup>		5.5				
TMP 12 EO								5					
GLY 12 EO											4		
OHN, mg	60	59.4	58.5	58.8	62	62	60.6	60	62	59	61.9	61	60.5
KOH/g													
AN, mg	1.5	0.6	1.4	1.8	1.2	1.3	1.3	1.3	0.9	0.9	0.9	1	1.1
KOH/g													

(1) Monoethylene glycol  
(2) Diethylene glycol  
(3) Monopropylene glycol  
(4) Trimethylolpropane  
(5) Triethanolamine  
(6) Pentaerythritol  
(7) Demineralized

In this table, the product A is a polyadipate  
5 sold by Witco Corporation under the name "Fomrez 60  
LV", which is prepared without use of ethoxylated  
polyalkanolamine; the product B is prepared from  
nonethoxylated triethanolamine. The ethoxylated  
triethanolamine comprising a small amount of potassium  
10 without removal at the end was used for all the  
products C, D, E, F, I, J, K, L and M; for the product  
G, the potassium was removed by addition of 2% of  
magnesium silicate (sold by Hoechst under the name  
"Ambosol C"), stirring for 2 hours at 100-110°C with

nitrogen at the surface and then filtering through paper.

c) Preparation of the foams

One of the polyesters A to M in Table II is 5 mixed manually using a rotary stirrer with 80/20 toluylene diisocyanate (TDI), which is a mixture of 2,4-TDI and 2,6-TDI in an 80/20 ratio. The amount of polyisocyanate employed is stoichiometric with respect to all the ingredients capable of reacting with the 10 isocyanate functional group (index 100).

The mixture comprises water and a surfactant: "Niax silicon surfactant SE 232 or L 534", sold by the company "Witco Corporation".

The various formulations per 100 parts by 15 weight of polyester necessary in order to obtain a foam with a density equal to approximately 30 kg/m<sup>3</sup> are given in Table III below.

In the case of the polyester A, two tests were carried out:

20 - one (A1) in the presence of two tertiary amines conventionally used as catalyst: N-ethylmorpholine (NEM) and hexadecyldimethylamine (HDDMA), and - the other (A2) in the absence of catalyst.

With the polyester H, a formulation with 25 another conventional amine catalyst: DB = dimethylbenzylamine (Test H1), and a noncatalyzed formulation (Test H2) are also given.

Tests B, C1, D, E1, F1, G, I, J and K were carried out without addition of separate tertiary amine 30 catalysts. In Tests C2, E2, F2, L and M1, an organometallic catalyst, stannous octoate, was added. In Test M2, a small amount of tertiary amine was introduced.

The cream time (time necessary for the 35 beginning of the foaming) and the rise time (time necessary in order to obtain the end of the foaming) were measured. The stability of the foam was also evaluated by assessing the collapse at the end of rise. The quality of the foam was also evaluated after

maturing for 30 min at 90-100°C, followed by 24 hours at 23-25°C. The visual appearance is given, as well as the number of cells per cm when the foam is satisfactory.

TABLE III

Formulation	A1	A2	B	C1	C2	D	E1	E2	F1	F2	G	H1	H2	I	J	K	L	M1	M2
water	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	
Niax SE 232	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
Niax L 534	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
NEM	1.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
HDDMA	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
DB(1)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.6	
Starious	-	-	-	-	0.05	-	-	0.05	-	-	-	-	-	-	-	0.05	0.05	-	
octocate																			
Cream time, s	12	240	85	20	16	18	15	15	12	15	16	200	17	14	15	20	20	16	
Rise time, s																			
Collapse at the end	83	>>300	>300	125	120	100	96	87	98	90	95	78	>>300	112	95	113	110	115	
Appearance of the foam	none	total	very high	slight cracked	slight cracked	slight cracked	none	slight cracked	none	slight cracked	none	total	slight cracked	none	none	none	none	none	
Number of cells/cm <sup>3</sup>	na*	na*	na*	na*	na*	na*	na*	na*	na*	na*	na*	na*	na*	na*	na*	na*	na*	na*	
Amine smell	strong	none	none	none	none	none	none	none	none	none	strong	none	none	none	none	none	none	slight	

(1) Dimethylbenzylamine

\* not applicable: there is collapse of the foam

These tests show that the polyesterpolyols C, D, E, F, G, I, J, K, L and M which comprise polyethoxylated triethanolamine make it possible to obtain, without it being necessary to add a separate tertiary amine

5 catalyst, foams having a reactivity similar to that of the standard formulation A1 in which a separate catalyst composed of two tertiary amines was used. Furthermore, the foams obtained do not have an amine smell perceptible to the nose.

10 The tests carried out with the polyesterpolyols J and K show that it is possible to do without amine catalyst. Comparison of Tests C1 and C2, E1 and E2, and F1 and F2 show [sic] that when the gelling reaction is not sufficiently catalyzed, addition of a small amount of

15 organometallic catalyst, which has the advantage of not introducing free amine, makes it possible to obtain a foam which does not collapse. Tests L and M1 confirm this behavior. Test M2 shows that it is optionally possible to obtain a good foam by using a tertiary amine but in a markedly lower amount than in a conventional formulation (Tests A1 and H1).

20 Comparison of the foams obtained with the polyesterpolyols F1 and G shows that the potassium is not the cause of the observed catalytic effect.

25 Test B shows that the catalytic effect according to the invention is not produced when the polyesterpolyol incorporates only a nonethoxylated triethanolamine.

30 Tests A2 and H2 show that the catalytic effect according to the invention is not produced when no catalyst is employed at the time of mixing and when a polyesterpolyol obtained without incorporation of ethoxylated triethanolamine is used.

**CLAIMS**

1. Process for the manufacture of a polyurethane foam by reaction of at least one polyesterpolyol and of at least one polyisocyanate in the presence of a 5 foaming agent and of a catalyzing agent, such a polyesterpolyol having been obtained beforehand by reaction of an acid reactant A, comprising at least one aliphatic or aromatic polyacid with a functionality at least equal to 2, with at least one polyol P2 with a 10 functionality equal to 2 and at least one polyol P3 with a functionality at least equal to 3 and subsequently being denoted by AP2P3, characterized in that the catalyzing agent is at least partially composed of at least one amine polyesterpolyol AP2P3, 15 in which at least a portion of the polyol P3 is composed of at least one polyoxyalkylenated polyalkanolamine having at least one tertiary amine functional group, the alkanol radicals of the said polyalkanolamine being C<sub>1</sub>-C<sub>6</sub> radicals, the alkylene 20 oxide units being C<sub>2</sub>-C<sub>4</sub> units and the statistical mean of the number N of alkylene oxide units per polyoxyalkylated polyalkanolamine molecule being equal to f × x, f being the number of hydroxyl functional groups per polyalkanolamine molecule and x being a 25 number between 1 and 10 inclusive.

2. Process according to Claim 1, characterized in that the foaming agent is water.

3. Process according to Claim 2, characterized in that the amine polyesterpolyol(s) AP2P3 is (are) the 30 only amine catalyst(s) of the catalyst agent.

4. Process according to either of Claims 2 and 3, characterized in that the catalyst agent comprises, in addition to the amine polyesterpolyol(s) AP2P3, at least one catalyst of organometallic type.

35 5. Process according to one of Claims 1 to 4, characterized in that the polyalkanolamine at least partially constituting the polyol P3 is a polyamine.

6. Process according to Claim 5, characterized in that all the amine functional groups of the polyamine are tertiary.

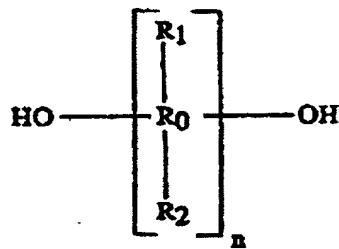
7. Process according to one of Claims 1 to 6, 5 characterized in that the polyalkanolamine at least partially constituting the polyol P3 is a tertiary monoamine.

8. Process according to one of Claims 1 to 7, 10 characterized in that the alkanol radicals of the polyalkanolamine(s) are C<sub>2</sub>-C<sub>3</sub> radicals and the alkylene oxide units are taken from the group formed by ethylene oxide, propylene oxide and their mixtures, x being a number between 2 and 5 inclusive.

9. Process according to one of Claims 1 to 7, 15 characterized in that, in the amine polyesterpolyol AP2P3, the molar ratio of the polyoxyalkylenated polyalkanolamine(s) to all the other polyols used for the reaction with the acid reactant A is between 1/99 and 50/50.

20 10. Process according to one of Claims 1 to 9, characterized in that the polyol P2 comprises at least one glycol chosen from the group formed by monoethylene glycol, diethylene glycol and polyethylene glycols with an order greater than 2.

25 11. Process according to one of Claims 1 to 10, characterized in that the polyol P2 comprises at least one branched glycol of formula:



in which formula:

30 - R<sub>0</sub> represents, independently in each [R<sub>1</sub>R<sub>0</sub>R<sub>2</sub>] unit, a carbon atom, a C<sub>6</sub> alicyclic radical, a phenyl radical or a heterocyclic radical comprising 4 to 6 atoms which is saturated or unsaturated, the heteroatom being O or N;

- R<sub>1</sub> and R<sub>2</sub> represent, independently in each [R<sub>1</sub>R<sub>0</sub>R<sub>2</sub>] unit and independently of one another, a hydrogen atom, a linear C<sub>1</sub>-C<sub>6</sub> alkyl radical, a branched C<sub>3</sub>-C<sub>6</sub> radical, a C<sub>6</sub> alicyclic radical or an aryl radical;
- 5 - with the proviso that, if R<sub>0</sub> is not a ring in any of the [R<sub>1</sub>R<sub>0</sub>R<sub>2</sub>] units, R<sub>1</sub> and/or R<sub>2</sub> is (are) different from H in at least one of the [R<sub>1</sub>R<sub>0</sub>R<sub>2</sub>] units;
- 10 - n is an integer between 1 and 8 (inclusive), with the proviso that, if n is greater than or equal to 4, the number of the carbon atoms in the combined R<sub>0</sub>, R<sub>1</sub> and R<sub>2</sub> radicals is greater than 8 in total.

12. Process according to one of Claims 1 to 10, characterized in that the polyol P3 is composed entirely of one or more polyoxyalkylenated polyalkanolamine(s).

15. Process according to one of Claims 1 to 11, characterized in that the polyol P3 comprises at least one polyoxyalkylenated polyalkanol obtained by oxyalkylation from a hydroxylated component taken from the group formed by trimethylolethane, trimethylolpropane, ditrimethylolpropane, pentaerythritol, dipentaerythritol, glycerol, hexane-1,2,6-triol, butane-1,2,4-triol, sorbitol, tris(2-hydroxyethyl) isocyanurate and their mixtures, the number of alkylene oxide units per polyoxyalkylenated polyalkanol molecule being, per hydroxyl functional group, as a statistical mean, between 1 and 10 inclusive.

20. Process according to one of Claims 1 to 13, characterized in that the acid reactant A comprises at least one diacid taken from the group formed by adipic acid and phthalic anhydride.

25. 15. Process according to one of Claims 1 to 14, characterized in that the acid reactant A comprises at least one branched acid having a functionality greater than or equal to 2.

16. Process according to Claim 15, characterized in that the branched acid is a dimer of an unsaturated C<sub>12</sub>-C<sub>24</sub> fatty acid.

17. Amine polyesterpolyol AP2P3 capable of being used in the process according to one of Claims 1 to 16, the said polyesterpolyol AP2P3 being obtained by reaction of an acid reactant A, comprising at least one aliphatic or aromatic polyacid with a functionality at least equal to 2, with at least one polyol P2 with a functionality equal to 2 and at least one polyol P3 with a functionality at least equal to 3, characterized in that at least a portion of the polyol P3 is composed of at least one polyoxyalkylenated tertiary polyalkanolmonoamine, the alkanol radicals of the said polyalkanolmonoamine being C<sub>1</sub>-C<sub>6</sub> radicals, the alkylene oxide units being C<sub>2</sub>-C<sub>4</sub> units and the statistical mean of the number of alkylene oxide units per hydroxyl functional group of the polyalkanolmonoamine molecule being between 1 and 10 inclusive, the polyol P2 not comprising monoethylene glycol.

18. Amine polyesterpolyol AP2P3 capable of being used in the process according to one of Claims 1 to 16, the said amine polyesterpolyol AP2P3 being obtained by reaction of an acid reactant A, comprising at least one aliphatic or aromatic polyacid with a functionality at least equal to 2, with at least one polyol P2 with a functionality equal to 2 and at least one polyol P3 with a functionality at least equal to 3, characterized in that at least a portion of the polyol P3 is composed of at least one polyoxyalkylenated polyalkanolamine having at least one tertiary amine functional group, the alkanol radicals of the said polyalkanolpolyamine being C<sub>1</sub>-C<sub>6</sub> radicals, the alkylene oxide units being C<sub>2</sub>-C<sub>4</sub> units and the statistical mean of the number N of alkylene oxide units per polyalkanolpolyamine molecule being equal to f × x, f being the number of hydroxyl functional groups per polyalkanolamine molecule and x being a number between 1 and 10 inclusive.

19. Amine polyesterpolyol AP2P3 according to Claim 18, characterized in that all the amine functional groups of the polyamine are tertiary.

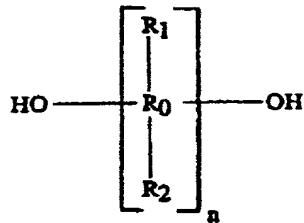
20. Amine polyesterpolyol AP2P3 according to one of 5 Claims 17 to 19, characterized in that the alkanol radical of the polyalkanolamine(s) is a C<sub>2</sub>-C<sub>3</sub> radical and the alkylene oxide unit is taken from the group formed by ethylene oxide, propylene oxide and their mixtures.

10 21. Amine polyesterpolyol AP2P3 according to one of Claims 17 to 20, characterized in that the molar ratio of the polyoxyalkylenated polyalkanolamine to all the other polyols used for the reaction with the acid reactant A is between 1/99 and 50/50.

15 22. Amine polyesterpolyol AP2P3 according to Claim 17, characterized in that the polyol P2 comprises at least one glycol chosen from the group formed by diethylene glycol and polyethylene glycols with an order greater than 2.

20 23. Amine polyesterpolyol AP2P3 according to Claim 18, characterized in that the polyol P2 comprises at least one glycol taken from group formed by monoethylene glycol, diethylene glycol and polyethylene glycols with an order greater than 2.

25 24. Amine polyesterpolyol AP2P3 according to one of Claims 17 to 23, characterized in that the polyol P2 comprises at least one branched glycol of formula:



in which formula:

30 - R<sub>0</sub> represents, independently in each [R<sub>1</sub>R<sub>0</sub>R<sub>2</sub>] unit, a carbon atom, a C<sub>6</sub> alicyclic radical, a phenyl radical or a heterocyclic radical comprising 4 to 6 atoms which is saturated or unsaturated, the heteroatom being O or N;

- R<sub>1</sub> and R<sub>2</sub> represent, independently in each [R<sub>1</sub>R<sub>0</sub>R<sub>2</sub>] unit and independently of one another, a hydrogen atom, a linear C<sub>1</sub>-C<sub>6</sub> alkyl radical, a branched C<sub>3</sub>-C<sub>6</sub> radical, a C<sub>6</sub> alicyclic radical or an aryl radical;
- 5 - with the proviso that, if R<sub>0</sub> is not a ring in any of the [R<sub>1</sub>R<sub>0</sub>R<sub>2</sub>] units, R<sub>1</sub> and/or R<sub>2</sub> is (are) different from H in at least one of the [R<sub>1</sub>R<sub>0</sub>R<sub>2</sub>] units;
- 10 - n is an integer between 1 and 8 (inclusive), with the proviso that, if n is greater than or equal to 4, the number of the carbon atoms in the combined R<sub>0</sub>, R<sub>1</sub> and R<sub>2</sub> radicals is greater than 8 in total.

25. Amine polyesterpolyol AP2P3 according to one of 15 Claims 17 to 24, characterized in that the polyol P3 is composed entirely of one or more polyalkanolamine(s).

26. Amine polyesterpolyol AP2P3 according to one of 20 Claims 17 to 24, characterized in that the polyol P3 comprises at least one polyoxyalkylenated polyalkanol obtained by oxyalkylenation from a hydroxylated component taken from the group formed by trimethylolethane, trimethylolpropane, ditrimethylolpropane, pentaerythritol, dipentaerythritol, glycerol, hexane-1,2,6-triol, butane-1,2,4-triol, sorbitol, 25 tris(2-hydroxyethyl) isocyanurate and their mixtures, the number of alkylene oxide units per hydroxyl functional group being, as a statistical mean, between 1 and 10 inclusive.

27. Amine polyesterpolyol AP2P3 according to one of 30 Claims 17 to 26, characterized in that the acid reactant A comprises at least one diacid taken from the group formed by adipic acid and phthalic anhydride.

28. Amine polyesterpolyol AP2P3 according to one of 35 Claims 17 to 27, characterized in that the acid reactant A comprises at least one branched acid having a functionality greater than or equal to 2.

29. Amine polyesterpolyol AP2P3 according to Claim 28, characterized in that the branched acid is a dimer of an unsaturated C<sub>12</sub>-C<sub>24</sub> fatty acid.

30. Polyurethane foam obtained by the process according to one of Claims 1 to 16.
31. Use of the foam according to Claim 30 for the production of elements intended to equip the passenger 5 compartment of a motor vehicle.

## ABSTRACT

The invention concerns a method for making a  
10 polyurethane foam by reacting at least a polyester  
polyol with at least a polyisocyanate in the presence  
15 of a foaming agent and a catalytic agent, such a  
polyester polyol having been previously obtained by  
reacting a reactive acid A comprising at least an  
20 aliphatic or aromatic polyacid with functionality not  
less than 2 with at least a polyol P2 with  
functionality equal to 2 and at least an aliphatic or  
aromatic polyacid with functionality not less than 2  
25 with at least a polyol P2 with functionality equal to  
2 and at least a polyol P3 with functionality not  
less than 3, being thereafter called AP2P3, wherein  
30 the catalytic agent at least partly consists of at  
least one amine polyester polyol AP2P3, wherein at  
least part of polyol P3 consists of at least a  
40 polyoxyalkylene polyalkanolamine having at least a  
tertiary amine function, the alkanol radicals of said  
45 polyalkanolamine being C1-C6, the alkylene oxide  
units being C2-C4 and the statistical mean of the  
50 number N of alkylene oxide units per polyoxyalkylene  
polyalkanolamine being equal to  $f \times X$ , f being the  
number of hydroxyl functions per polyalkanolamine  
55 molecule and X being a number ranging between 1 and  
10, inclusively.

## **Declaration and Power of Attorney for Patent Application**

As the below named inventors, We hereby declare that:

Our residences, post office addresses and citizenship are as stated below next to our names; We believe we are the original, first and joint inventors of the invention which is described and claimed and for which a patent is sought on the invention entitled:

PROCESS FOR THE MANUFACTURE OF POLYURETHANE FOAM, AMINE POLYESTERPOLYOL USED IN THIS PROCESS AND FOAM OBTAINED

the specification of which (check one)

is attached hereto,

was filed on \_\_\_\_\_ and accorded serial number \_\_\_\_\_ and  
was amended on \_\_\_\_\_.

We hereby state that we have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We acknowledge the duty to disclose information which is material to the examination of this application in accordance with 37 CFR § 1.56(a).

We hereby claim foreign priority benefits under 35 USC §119 or §365 of any foreign application(s) for patent or inventor's certificate, or §365 of any PCT international application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

**Prior Foreign Application(s):**

Number	Country	Day/Month/Year	Priority	Claimed
PCT/FR99/01176	PCT	18 May 1999	YES	
98 06806	France	29 May 1998	YES	

We hereby claim the benefit under 35 USC §119(e) of any United States provisional application(s) listed above:

**Application Number** **Filing Date**

We hereby claim the benefit under 35 USC §120 of any United States application(s), or any §365<sup>®</sup> of any PCT international application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of 35 USC §112, We acknowledge the duty to disclose material information as defined in 37 CFR §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

Prior U.S. Applications:  
**Serial No.**      **Filing Date**      **Status (patented, pending, abandoned)**

We hereby appoint the following attorney's and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: **Raymond D. Thompson - Reg. No. 30,695, Daniel Reitenbach - Reg. No. 30,970, and Shirley S. Ma - Reg. No. 44,216.**

Address all telephone calls to: **Shirley S. Ma of Crompton Corporation at (203)573-3313.**

Address all correspondence to: **CROMPTON CORPORATION**  
199 Benson Road  
Middlebury, CT 06749

We hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

(1)	FULL NAME OF INVENTOR	GHEQUIERE, DENIS	
	CITIZENSHIP	FRENCH	
	RESIDENCE ADDRESS	29, rue Madeleine Fosse, F-27370, Tourville la Campagne, France	
	POST OFFICE ADDRESS	Same as Above	
	SIGNATURE	DATE	

(2)	FULL NAME OF INVENTOR	DUMONT, RéMY	
	CITIZENSHIP	FRENCH	
	RESIDENCE ADDRESS	37, rue du Point du jour, F-27370 Thuit Signol, France	
	POST OFFICE ADDRESS	Same as Above	
	SIGNATURE	DATE	